# Evolution of health and climate relevant in-cylinder diesel soot characteristics investigated with on-line aerosol mass spectrometry

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Despite increasingly stringent emission legislations, heavy-duty (HD) diesel vehicles remain as major emitters of black carbon, commonly referred to as soot. A new and effective method to reduce $NO_x$ pollutants from HD diesel engines is exhaust gas recirculation (EGR). When EGR is applied, exhaust gases are recirculated to the engine inlet air. This technique lowers the $O_2$ availability during combustion and subsequently the rate at which $NO_x$ is formed in combustion. However, when EGR is applied soot emissions rapidly increase and the soot characteristics changes. Understanding the processes responsible for this increase is essential for continued reductions in soot emissions from diesel engines. It is therefore important to understand the evolution of soot concentrations and characteristics in the cylinder as these complex combustion processes dictates the soot emission levels and shapes the properties of the emitted soot.

To study the relationship between engine combustion conditions and soot characteristics, a modern HD diesel engine with EGR was run at 1200 rpm and low load. A fast gas-sampling valve (FSV) was mounted on the engine to extract in-cylinder soot particles at well-defined parts of the combustion cycle (crank angle degrees). The extracted aerosol was diluted and the chemical composition of the particles characterized with a soot-particle aerosol mass spectrometer (SP-AMS, Onash et al., 2012). In the SP-AMS, refractory black carbon (rBC) was characterized by vaporization of the particles using an Nd-YAG laser (1064 nm) heating the particles to ~4000 K followed by electron impact ionization (70 eV) and detection of ion fragments in a time-of-flight mass spectrometer. Non-refractory species (e.g. organic components) were flash vaporized on a porous-tungsten vaporizer heated to ~900 K, followed by ionization and detection. With this procedure, the composition of the refractory soot core and non-refractory coating can be determined separately.

The results show that the altered combustion conditions induced by EGR strongly influence both soot formation and oxidation. Related to the fuel injection timing, the highest in-cylinder concentration of rBC occur at 0% EGR and is 10 times higher than the maximum in-cylinder concentration at 64% EGR. On the other hand, soot oxidation rates are significantly reduced when EGR is applied and exhaust soot emissions increase from approximately 140 µg/m$^3$ at 0% EGR to 5500 µg/m$^3$ at 64% EGR.

The in-cylinder measurements reveal differences in the chemical properties of both soot core and coating as EGR increase (Fig.1). With EGR the Fullerene-carbon signal ($C_{32}$-$C_{58}$), the PAH-fraction of Organic Aerosol and angstrom absorption coefficient is higher in the early combustion phase. SP-AMS fullerene-carbon signals have been associated with less mature soot (Onasch et al. 2015). Thus, introduction of EGR may result in a significantly slower soot maturation process e.g. resulting in changes of the soot core nanostructure.

When EGR is applied, the organic fraction of oxygen containing ion fragments of the soot coating is higher in the early combustion phase while lower in the late combustion and exhaust. The lower fraction in the exhaust is likely caused by much lower $O_2$ concentration in the late combustion cycle with EGR compared to 0% EGR. However, when EGR is introduced the refractory $CO_2^+$ signal increases relative to rBC. Refractory $CO_2^+$ has been associated with tightly bound surface oxides and may therefore be a result of altered soot maturity.

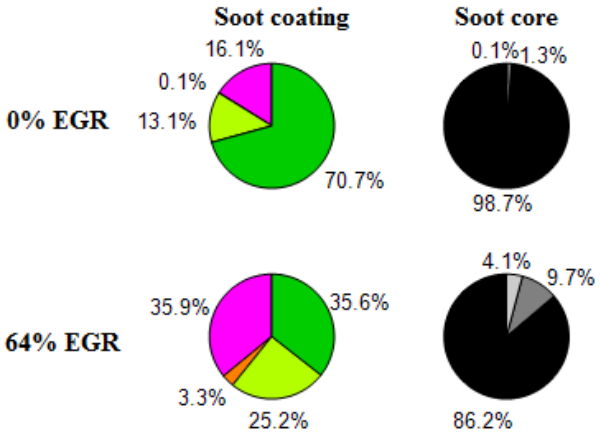


**Figure 1:** Difference in chemical composition of soot coating (left) and core (right) in the early combustion phase at 0% EGR and 64% EGR. $C_xH_y$ (green), $C_xH_{y<x}$ (light green), $C_xH_yO_z$ (magenta), PAHs (orange), $C_{1\text{-}5}$ (black), $C_{6\text{-}31}$ (dark grey), $C_{32\text{-}58}$ (light grey).

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